Photochemical surface modification and characterization of double-decker-shaped polysilsesquioxane hybrid thin films

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The surface modification of a double-decker-shaped polysilsesquioxane (DDPSQ) film by deep ultraviolet (UV) irradiation (λ = 185 and 254 nm) was studied in the presence of atmospheric oxygen at room temperature. The change in the surface structure of a DDPSQ hybrid film was observed by means of contact angle measurements, Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM). Exposure to deep UV light was found to convert the surface of DDPSQ film from hydrophobic to hydrophilic due to the formation of silanol groups (Si–OH) on the DDPSQ film. Measurements of FT-IR and XPS indicate that the Si–O–Si cage structure of DDPSQ was converted to the Si–O–Si network structure of SiO2 through cleavage of the Si–O–Si cage with deep UV irradiation. The irradiated DDPSQ film surface is very smooth with a root-mean-square (RMS) roughness of 0.34 nm. Moreover, to demonstrate the effect of surface modification of a DDPSQ film on the adhesion of metals, we fabricated silver (Ag) micropatterns on the deep UV modified DDPSQ film by laser-induced pyrolysis of a film prepared from liquid-dispersed Ag nanoparticles. The Ag micropatterns show an excellent adhesion to the modified DDPSQ surface as assessed by the Scotch tape test.

Introduction

Hybrid organic–inorganic materials have attracted considerable interest during the past few decades because they offer the opportunity to prepare high-performance multifunctional advanced materials through the combination of properties of organic and inorganic segments.1–5 Therefore, numerous classes of hybrid materials such as three-dimensional sol–gel materials,6,7 preceramic polymers,8 inorganic–organic blends,9 intercalation, and exfoliation of layered silicates by organic polymers10 have been developed for numerous applications in many areas: optics; electronics; ionics; mechanics; energy; environment; biology; medicine for example, as membranes and separation devices; functional smart coatings; fuel and solar cells; catalysts; sensors; light emitting devices (LEDs) etc.11 Recently, a new approach for the construction of nanohybrid materials based on polyhedral oligomeric silsesquioxane (POSS) as an inorganic moiety has attracted a lot of interest.12–14 POSS is a cube-octameric molecule with an inner inorganic silicon and oxygen (Si–O–Si) framework that is externally covered by organic substituents.15,16 POSSs are ideal building blocks for the construction of organic–inorganic hybrid materials. By changing the POSS structure, for example, organic side chains and ring structure, nanoarchitectures of hybrid materials can be easily controlled. Thus far, numerous POSS-based hybrid materials have been prepared by incorporation of POSS moieties in a variety of polymeric materials such as polyolefins,17 polynorbornenes,18 styrenics,19 acrylics,20 polysiloxanes,21 epoxies,22 polyimides,23 and polyurethanes24 via polymerization, blending, and grafting. The incorporation of POSS units into polymeric materials can lead to substantial improvements in polymer properties including increased thermal stability, oxidation resistance, surface hardness, and mechanical properties, as well as reductions in flammability, heat evolution, and viscosity during processing.

Double-decker-shaped silsesquioxanes (DDSQs) are a new family of silsesquioxanes consisting of nanometre-sized Si–O–Si cage structures functionalized with a wide variety of organic substituents.13,25–28 DDSQ-based hybrid polymers (double-decker-shaped polysilsesquioxane, DDPSQ, Fig. 1) possess many fascinating properties such as high thermal stability, good mechanical properties, low dielectric constant, excellent transparency, excellent flexibility, and so on.29 Due to these fascinating properties DDPSQ can be used as a candidate substrate for flexible or polymer electronics such as flexible flat panel and wearable displays, smart cards, and information tags etc. For such applications drawing of conductive metal (Au, Cu, Ag) patterns on a DDPSQ substrate is required. However, the surface of DDPSQ film is hydrophobic resulting in poor adhesion to metals. Consequently, surface modification of the DDPSQ polymer can solve this polymer–metal adhesion problem like other engineering polymers such as polyimide and polytetrafluoroethylene (PTFE).29–32 Surface modification of polymers is a convenient and efficient process for producing polymers with tailored physicochemical properties such as wettability, adhesion, lubrication, conductivity and biocompatibility. The common approaches to the surface modification of polymers include surface chemical treatment, flame treatment, plasma treatment, corona discharge treatment, and irradiation treatment such as X-ray, γ-ray, UV, laser, electron beam, and ion...
beam etc. Surface modification of DDPSQ by UV irradiation has several advantages such as that the technique is simple, fast, easy to implement, reliable, and cost-effective. Moreover, creation of microscopic hydrophilic and hydrophobic patterned surfaces by UV irradiation using a photomask is also advantageous. Herein, we report surface modification of DDPSQ hybrid film by deep UV irradiation (λ = 185 and 254 nm) in the presence of atmospheric oxygen at room temperature. Surface modification of DDPSQ hybrid films was studied by means of contact angle measurements, Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Moreover, we fabricated silver (Ag) micropatterns on the deep UV modified DDPSQ film by laser-induced pyrolysis of a film prepared from liquid-dispersed Ag nanoparticles and investigated its adhesion characteristics by the Scotch tape test.

**Experimental section**

Sila-DEC (DDPSQ5002, \( M_w = 6.63 \times 10^3, M_w/M_n = 2.29 \)) was obtained from Chisso Petrochemical Co., Japan. A thin film of DDPSQ on solid substrates such as glass, silicon and quartz was prepared using a spin-coater (Mikasa Spin Coater, 1H-D7, Mikasa Co. Ltd, Japan) from a solution (10 wt%) of DDPSQ in toluene at 2000 rpm for 30 s and the obtained film was baked at 110 °C for 1 min in order to evaporate the solvent. The thickness of the DDPSQ film was estimated to be 412 nm as measured by a surface profiler (Dektak I ST, ULVAC). Exposure to deep UV light was performed with a low-pressure mercury lamp of 3 cm in diameter and approximately 30 cm in length mounted in an irradiation chamber (Photo Surface Processor, SEN Lights Co.). The low-pressure mercury lamp generated UV irradiation wavelengths of \( \lambda = 185 \) and 254 nm with an intensity of 16 mW cm\(^{-2} \) at distance of 10 mm to the UV source. The DDPSQ surfaces were irradiated at ambient conditions in air with an intensity of 16 mW cm\(^{-2} \) at distance of 10 mm to the UV source. Two different oxygen flow rates such as 1.0 m\(^3\) min\(^{-1} \) and 0.2 m\(^3\) min\(^{-1} \) were used during photoradiation of DDPSQ films. The wettability of a DDPSQ surface was examined by measurements of contact angles. Contact angles of water on DDPSQ surfaces were measured by the sessile drop method with CA-X contact angle meter (Kyowa Interface Science Co. Ltd) at 20 °C and ambient humidity. The contact angles were the average of five measurements at different positions for one sample. FT-IR spectra were measured with a Jasco FT-IR-4200 in the range 4000–500 cm\(^{-1} \) with a spectral resolution of 2 cm\(^{-1} \). UV absorption spectra were measured by a JascoV-670 spectrophotometer. XPS analysis was performed using an ESCA 5300 X-ray photoelectron spectrometer (Parkin-Elmer), which was operated at 6 kV and 35 mA with Mg K\( \alpha \) X-ray source and at less than 7.0 \( \times \) 10\(^{-9} \) torr. The take-off angle was fixed at 45°. All binding energies in XPS measurements were referenced to the C 1s peak for neutral carbon, which was assigned a value of 285.0 eV. We used the D, T and Q convention for identifying the silicon atoms with 2, 3 and 4 oxygens attached respectively. Atomic force microscopy (AFM) images were recorded with a Seiko SPI3800N microscope (SPA-400, Seiko Instruments Inc.) in a tapping mode (cantilever type: SI-DF20, \( f = 139 \) kHz, spring constant = 16 N m\(^{-1} \), and aluminum coating). Ag nanometal ink was purchased from ULVAC Technologies Inc. and used as received. The nanometal ink is produced by the gas evaporation method (gas phase condensation) where Ag nanoparticles with an average particle size of 4.5 nm are individually dispersed in tetradecane. The nanoparticle surfaces were modified with organic surfactants to prevent agglomeration during preparation. A continuous wave Ar ion laser (wavelength: 488 nm and 514.5 nm, MELLES GRIOT 543–300A) was introduced into a microscope and focused onto the precursor film through an objective lens. The focused laser beam was scanned by a computer-controlled \( x-y-z \) stage. During drawing of a micropattern, the shape was observed by a charge-coupled device (CCD) camera. The adhesion strength of Ag micropatterns on a DDPSQ film was evaluated using the Scotch tape test.

**Results and discussion**

**Surface modification of a DDPSQ film by deep UV irradiation**

The modification of DDPSQ surfaces by deep UV irradiation was studied by wetting experiments. Changes in static water contact angles of uniformly photoradiated DDPSQ surfaces in the presence of oxygen using a flow rate of 1.0 m\(^3\) min\(^{-1} \) and 0.2 m\(^3\) min\(^{-1} \) are plotted in Fig. 2. The formation of ozone and molecular oxygen by exposure to deep UV light is enhanced by increasing the oxygen flow rate. Before UV exposure, the water contact angle of a DDPSQ surface was 104.5° (hydrophobic) due to the presence of organic moieties such as methyl, phenyl etc. In both cases, as photoradiation was prolonged, the water contact angle of the DDPSQ surface gradually decreased and the degree of hydrophilicity strongly depends on the oxygen flow rates. The most remarkable decrease was observed for the oxygen flow rate of 1.0 m\(^3\) min\(^{-1} \), that is to say, the contact angle became less than 5° after irradiation for 5 min, indicating that the photoradiated DDPSQ surface became completely hydrophilic due to the

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**Fig. 1** The chemical structure of a double-decker-shaped polysilsesquioxane (DDPSQ5002).
formation of silanol (Si–OH) groups. However, in the case of an oxygen flow rate of 0.2 m$^3$ min$^{-1}$, the photoirradiated DDPSQ surface showed a contact angle of 60° indicating incomplete photodegradation of organic moieties of DDPSQ and further changes in the contact angles were observed at longer irradiation time (e.g., 30 min). After irradiation for 30 min, the contact angle was 22°. But, no further changes of the contact angles could be detected using an oxygen flow rate of 1.0 m$^3$ min$^{-1}$ at that irradiation time.

FT-IR spectroscopy has been used for detecting the formation of Si–OH groups during photoirradiation of a DDPSQ film and also monitoring the kinetics of photodegradation. Fig. 3 shows the FT-IR spectra of a DDPSQ film as a function of deep UV irradiation time. The irradiated DDPSQ film shows a broad peak centered at 3300 cm$^{-1}$ which could be attributed to vibration modes of Si–OH and the absorbance of the Si–OH stretch increases gradually with deep UV irradiation time. This result is consistent with the gradual decrease in contact angle with irradiation time as shown in Fig. 2. Before exposure to UV, the DDPSQ film shows a sharp and intense Si–O–Si asymmetric stretching peak at 1122 cm$^{-1}$, which indicates the existence of a Si–O–Si cage framework of DDPSQ. With increasing UV exposure time this peak was diminished gradually indicating cleavage of the silsesquioxane (Si$_2$O$_3$) (T) cage moiety in DDPSQ film. After exposure to UV for 30 min, this peak broadened and shifted to a lower wavenumber, 1077 cm$^{-1}$, corresponding to the Si–O–Si network structure of SiO$_2$ (D). Thus, FT-IR measurement indicates that the Si–O–Si cage structure in DDPSQ is converted to a Si–O–Si network structure of SiO$_2$ via cleavage of the Si–O–Si cage and oxidation with loss of the alkyl/phenyl substituents upon UV irradiation in the presence of atmospheric oxygen. Moreover, other peaks exist and become progressively weaker after UV exposure: 1429 cm$^{-1}$, attributed to C=C stretching, 1260 cm$^{-1}$ to Si–C stretching, 805 cm$^{-1}$ to Si–O–Si bending, 2958 cm$^{-1}$ to asymmetric stretching to CH$_3$, and 2907 cm$^{-1}$ to CH$_3$ symmetric stretching. The kinetics of photodegradation of a DDPSQ film in the presence of oxygen were monitored by measuring the absorbance of Si–OH using flow rates of 1.0 m$^3$ min$^{-1}$ and 0.2 m$^3$ min$^{-1}$ (Fig. 4) and it is clear that generation of surface silanol groups is faster with an oxygen flow rate of 1.0 m$^3$ min$^{-1}$ and consistent with the results shown in Fig. 2.

UV absorption spectroscopy has been applied to monitor the photodecomposition of phenyl substituents of a DDPSQ film by deep UV irradiation. Fig. 5 shows the change in UV absorption spectra of a DDPSQ film on a quartz substrate as a function of UV exposure time and it is clear that absorption bands attributable to the π–π* transition of the phenyl ring gradually decreased as the UV exposure time increases. This fact indicates the removal of the phenyl moiety during photolysis of the DDPSQ film in the presence of oxygen. The removal of the phenyl/methyl substituents of a DDPSQ film by UV exposure is also confirmed by measuring the thickness of the DDPSQ film. Before UV exposure, the DDPSQ film had a thickness of 412 nm. However, after 30 min of UV exposure the thickness of the DDPSQ film was 380 nm, thus indicating decomposition of phenyl/methyl substituents of the DDPSQ film by UV irradiation.

XPS measurements were carried out in order to confirm the cleavage of the Si–O–Si (T) cage structure of the DDPSQ to a Si–O–Si network structure of D upon exposure to deep UV in the presence of O$_2$. The XPS binding energies of Si and silicon suboxides have been thoroughly studied for decades because of the importance of these materials in the semiconductor industry. The silicon-to-oxygen configuration has a particular Si(2p)
binding energy that is dependent on the number of oxygen atoms in the coordination shell. Studying the binding energy can therefore be used to monitor changes in the silicon configuration. Usually, the Si(2p) binding energy increases proportionally as the number of oxygen atoms coordinated to the silicon increases. Fig. 6a shows the Si(2p) XPS spectra for the DDPSQ film before UV exposure and after 30 min exposure to UV. Before UV exposure, the DDPSQ film had a Si(2p) binding energy of 102.22 eV, indicating the existence of a T cage moiety in the DDPSQ film. After UV exposure, the Si(2p) peak of the DDPSQ film had shifted to higher energy and centered at around 103.50 eV. This peak position corresponds nicely with literature values of 103.3–103.7 eV for SiO2.

Moreover, the nature of changes in the silicon configuration during UV exposure can be monitored through analysis of the O(1s) binding energy. Fig. 6b shows the O(1s) XPS spectra for the DDPSQ film before UV exposure and after 30 min exposure to UV. The pristine DDPSQ film showed an O(1s) peak at 532.0 eV indicating the presence of a T cage moiety. After UV exposure, the O(1s) peak of the DDPSQ film had shifted to higher energy and was centered at 533.20 eV. Again, the measured value corresponds quite well to the published data for SiO2. The XPS measurements also indicate large changes in the chemical composition of the irradiated DDPSQ film (Table 1). The carbon content decreased drastically whereas oxygen content increased tremendously after 30 min of UV exposure. The decrease in carbon content of the irradiated DDPSQ film suggests the removal of the organic portions of the DDPSQ as volatile compounds. Moreover, the silicon content remained almost constant, as silicon does not readily form volatile compounds under the experimental conditions.

On the basis of the FT-IR, UV, and XPS results, we propose the following mechanism for the formation of a Si–O–Si network structure (Scheme 1). Ozone, an active oxidizing agent is generated in situ from atmospheric oxygen by exposure to 185 nm UV light. The ozone produced subsequently photodissociates into molecular oxygen and atomic oxygen (a very strong oxidizing agent) upon exposure to 254 nm UV light. We assume that the initial step is the formation of a silicon radical through the cleavage of the Si–Ph and Si–Me bonds by atomic oxygen. Further reactions of the silicon radicals with oxygen leads to the formation of peroxy radicals, which rearrange to give silanol groups. Finally, silanol groups undergo a condensation reaction through the elimination of water molecules to produce a Si–O–Si network structure.

![Fig. 5 UV absorption spectra of a DDPSQ film with different UV exposure times.](image)

![Fig. 6 XPS spectra for the DDPSQ film before UV exposure and after exposure to UV for 30 min (a) Si(2p) and (b) O(1s).](image)

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<th>C (at.%)</th>
<th>O (at.%)</th>
<th>Si (at.%)</th>
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<tbody>
<tr>
<td>DDPSQ (before UV exposure)</td>
<td>60.87</td>
<td>21.97</td>
<td>17.16</td>
</tr>
<tr>
<td>DDPSQ (after UV exposure, 30 min)</td>
<td>4.12</td>
<td>67.78</td>
<td>28.10</td>
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**Scheme 1** Formation of Si–O–Si network structures by deep UV irradiation of a DDPSQ film.
The surface morphology was examined during UV irradiation of the DDPSQ films by AFM (Fig. 7). Before UV exposure, the DDPSQ hybrid film shows a homogeneous surface with a root-mean-square (RMS) roughness of 0.40 nm. After 5 min exposure to UV DDPSQ film surface is also found to be smooth with a RMS roughness of 0.34 nm.

Fabrication of Ag micropatterns on a modified DDPSQ film and their adhesion characteristics

To demonstrate the effect of surface modification of a DDPSQ film on adhesion of metals, we fabricated silver (Ag) micropatterns on the deep UV modified DDPSQ film by laser-induced pyrolysis of a film prepared from liquid-dispersed Ag nanoparticles and evaluated their adhesion strength by the Scotch tape test. Fig. 8 shows the process for fabrication of Ag micropatterns on a DDPSQ film by laser direct writing. First, a spin-coated DDPSQ film was subjected to deep UV irradiation as a result the DDPSQ surface became completely hydrophilic. This hydrophilic conversion facilitated spin-coating of Ag nanometal ink and simultaneously improved the adhesion between the polymer and the metal. Then, an Ag nanoparticle-dispersed film was prepared on the deep UV modified DDPSQ film by spin-coating of an Ag nanometal ink (50–60 wt%) at 2000 rpm for 30 s and the obtained film was dried by heating at 110 °C for 30 s.

Before laser irradiation, the thickness of the nanoparticle film was 730 nm, which was also determined by a surface profiler. Then, a laser beam was scanned on this film through an objective lens. The laser-irradiated region was converted to metal by the fast local thermal decomposition of organic surfactants and fusion of Ag nanoparticles. Finally, the unirradiated region was removed by immersing in n-hexane for 60 s. Fig. 9 shows the optical micrographs of the Ag micropatterns, where the laser beam was scanned under the following conditions: laser energy density = 2.13 kW cm⁻², objective lens magnification = 5×, scanning length = 1000 μm, interval between the scanning lines = 100 μm, and scanning speed = 100 μm s⁻¹. After the development process using n-hexane, the unirradiated region was removed easily and Ag micropatterns with a line width of about 75 μm have been achieved. The thickness of the Ag micropatterns after the development process under these conditions was determined to be ca. 350 nm.

The adhesion strength between the metal and the polymer substrate is one of the primary concerns for microelectronics applications. Thus, the adhesion strength of Ag micropatterns on a deep UV modified DDPSQ surface was evaluated by the Scotch tape test. 3M Scotch tape was applied to the Ag micropatterns, pressed down strongly, and then peeled off. After removal of the tape Ag micropatterns were observed using an optical microscope and it was found that the Ag microlines remained intact, no crack was found and they did not peel off from the DDPSQ surface (Fig. 10). This indicates that the Ag micropatterns exhibit an excellent adhesion to the modified DDPSQ film and are suitable for various practical applications.
Conclusion
Exposure to deep UV light was found to convert the surface of the DDPSQ film from hydrophobic to hydrophilic due to the formation of silanol groups (Si–OH) on the surface of the DDPSQ film. Measurements of FT-IR and XPS indicate that the Si–O–Si cage structure of DDPSQ was converted to the Si–O–Si network structure of SiO₂ through cleavage of Si–O–Si cage with deep UV irradiation. Ag micropatterns on the deep UV modified DDPSQ film exhibit excellent adhesion. Thus, DDPSQ films can be used as a potential substrate for fabrication of various lightweight, flexible microelectronic devices and will open entirely a new avenue in flexible printed electronics.

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References